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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

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For the President of the European Patent Office

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Braze alloy and the use of said braze alloy

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Braze alloy and the use of said braze alloy

TECHNICAL FIELD

The invention relates to a braze alloy according to claim 1, to a use of the braze alloy in pure form as a paste and foil or as a blend paste, as a braze tape or as a pre-sintered braze sheet according to claim 2, to a pre-sintered braze sheet, braze tape or a paste according to claim 3 and to a method of repairing an article according to claim 4 or 5.

STATE OF THE ART

The wide use of Nickel and Cobalt based superalloys allowed an increased turbine inlet temperature, which significantly helped to increase the turbine efficiency. Specially tailored superalloys were developed in order to make maximum use of material strength and temperature capability. Superalloys are cast in the polycrystalline (EQ), the directionally solidified (DS) and the single crystalline (SX) form. During operation of turbine components under high temperature conditions, various types of damages can occur. For example, cracks can result from thermal cycling, mechanical load and foreign object impact. Additionally, cracks and inclusions may be incurred during manufac-

ture. Furthermore, environmental attacks such as oxidation and corrosion can lead to local erosion and wall-thickness reduction of the components. Because the costs of components made from nickel-based superalloys are very high, especially components made from DS and SX superalloys, it is more desirable to repair these components than to replace them.

The following state of the art methods for repairing high temperature superalloys are generally known: EP-A1-1 258 545 discloses a method of isothermally brazing single crystal components with the full retention of the single crystalline microstructure in the brazed joint. US-A-5,732,467 discloses a method of repairing cracks on the outermost surface of an article having a directionally oriented microstructure and a superalloy composition. The repairing is done by coating the cleaned crack surface with a material featuring the same material composition as said article. Thereby the coated crack surface is subjected to an elevated temperature and isostatic pressure over a period of time sufficient to repair the crack surface without changing the crystalline microstructure of the parent article.

Additionally, a number of alternative brazing methods for repairing cracks or wide gaps in turbine components made from a cobalt and a nickel-base superalloy, are known such as US-A-5,666,643, US-A-4,381,944 or US-A-5,437,737. The braze material product is a blend of two powders, the low melting brazing powder and a parent superalloy powder as an additional filler material.

US 4,830,934 discloses a braze alloy powder mixture consisting of at least three distinct groups of alloy powders which together define a mixture composition which results in a significant improvement in strength and oxidation resistance over conventional braze alloy powders or mixtures.

Standard and commercially available braze powders, braze alloy blends and mixtures used for crack brazing comprise of a chemical composition which mainly aims for a high tensile strength. Furthermore the sufficient flow of the

braze alloy during brazing is of particular interest so that the total wetting of the cracks is guaranteed. The level of the melting point depressant (such as B or Si) must be balanced between a minimum level for a sufficient braze flow on one side, against a reasonable isothermal brazing time on the other side. The addition of heavy and refractory elements such as Cr, W and Ta, which guarantee the strength of the brazed area, are known to result in a more sluggish flowing braze alloy.

In most cases the braze-repaired gas turbine blading components undergo an re-coating process. Therefore the oxidation and corrosion resistance of the brazed area itself is of less interest as the braze joint or brazed tapes and pre-forms are protected by an overlay coating. Nevertheless, in some cases it is of interest to restore worn balding components at location where a re-coating process is not desired or where a local re-coating process is not applicable. In such cases a high oxidation and corrosion resistance of the brazed area, such as brazed joint or brazed tapes and pre-sintered braze sheets, is required.

Standard brazed cracks, brazed tapes or brazed pre-forms suffer from internal oxidation at elevated temperatures, which leads to an undesired material loss with proceeding time. Internal oxidation occurs due to the fact that the braze material or the braze mixture/blend used do not form a dense and stable oxide scale at the outer surface.

The content of the heavy and refractory elements in the braze alloy must be balanced in order to guarantee a dense oxide scale at elevated temperatures. Especially the ratio of the Aluminium to the Chromium content is known to have a significant influence on the oxide scale formation of the material and hence on the oxidation resistance. The consideration of a balanced Al/Cr content for optimum oxidation resistance applies for the usage of the pure braze alloy for crack brazing as well as for the usage of mixtures in a two-component braze powder blend. For tapes and/or pre-sintered braze sheet-material the overall nominal chemical composition resulting from the mixture of both powders must be balanced. Especially the precipitation of Chromium

rich borides in the braze-repaired tapes and sheets, which result in a local Cr-depletion in the matrix must be considered when tailoring a oxidation resistant braze tape or sheet.

SUMMARY OF INVENTION

It is aim of the present invention to develop a higher oxidation resistant braze alloy. It is the further the aim to produce braze-tapes (green material) and Pre-sintered Braze Sheets which are composed of a variable mixture of the new pure braze alloy and a parent superalloy filler with resulting enhanced oxidation resistance. As well, it is the aim of the present invention to find a method of repairing a gas turbine component by means of brazing with the inventive braze alloy pastes, braze tapes or the Pre-sintered Braze Sheets.

This objective is solved by a Nickel-based braze alloy comprising (wt.-%) 10-15% Cr, 4.5-6% Al, 0.05-0.3% Y, 8-12% Co, 0-4% W, 2.5-5% Ta, 2.0-3.5% B with Cr+Al > 15%, Cr/Al ≤ 3 and Al + Ta > 7.5%, Rest Nickel and unavoidable impurities.

According to the present invention the inventive braze alloy can either be used in pure form as a paste and foil or as a blend paste, as a braze tape or as a pre-sintered braze sheet. The pre-sintered braze sheet or braze tape comprises a mixture of filler material consisting of a nickel or cobalt superalloy and the braze alloy with at least 30 wt.-% braze alloy.

The braze alloy, the braze tapes and the pre-sintered braze sheets can be used in a braze repair method, e.g. for crack repair or wall thickness build up of ex-service gas turbine component in need of repair.

SHORT SUMMARY OF DRAWINGS

The invention is illustrated by the accompanying drawings, in which

Fig. 1 shows as an example a gas turbine blade,

Fig. 2 shows the oxidation attack of a standard pre-sintered braze sheets material at 950°C after 1000h and

Fig. 3, 4 shows the oxidation attack of the modified the pre-sintered braze sheets material at 950°C after 1600h.

The drawing shows only parts important for the invention.

PREFERRED EMBODIMENT OF THE INVENTION

The invention relates to a high temperature braze alloy composition, the use of the inventive braze alloy in pure form as a paste and foil or as a blend paste, as a braze tape or as a pre-sintered braze sheet and to a method of repairing cracks or gaps or for wall thickness restoration for example in or of a single crystal article made of a Nickel base superalloy by means of brazing using either the inventive braze alloy in pure form as a paste or as a blend paste, as a braze tape or as a pre-sintered braze sheet. Nickel base superalloys are know in the state of the art, e.g. from the document US-A-5,888,451, US-A-5,759,301 or from US-A-4,643,782, which is known as "CMSX-4". The single crystal article could possibly be a part of a gas turbine such as a blade and vane or a part of the burner chamber of the gas turbine. Fig. 1 shows as an example such an article 1 as blades or vanes comprising a blade 2 against which hot combustion gases are directed during operation of the gas turbine engine, a cavity, not visible in Fig. 1, and cooling holes 4, which are on the external surface 5 of the component 1 as well as on the platform 3 of the component. Through the cooling holes 4 cooling air is ducted during operation of the engine to cool the external surface 5. The external surface 5 is subjected to severe attack by oxidation, corrosion and erosion due to the intersection with hot combustion gases. In principle, the article 1 can be of equiaxed (cc), directionally solidified (DS) or single crystal (SX) structure. While the advantage of this invention is described with reference to a turbine blade or vane as shown in Fig. 1, the invention is generally applicable to any component which is in need of repair by means of high temperature brazing. Dur-

ing service the article is subjected to the hot environment of the gas turbine which leads to the deleterious effect of cracks, gap or wall thickness erosion in the surface of the article. One aim of the present invention is to find an oxidation resistant pre-sintered braze sheets or braze tape for example for the restoration of the wall thickness of such ex service hot gas path articles 1 of a land based gas turbine. The pre-sintered braze sheets are made of the braze tapes through sintering which are composed of a variable mixture of braze alloy, filler powder and binder through executing appropriate thermal pre-sintering cycles. The pre-sintered braze sheets (PSP) are free of binder and shall exhibit a very low grade of porosity. Pre-sintered braze sheets and related products are a sintered blend of braze alloy and superalloy powders available in various compositions, sizes and shapes.

Before applying the method of brazing as described below, a protective coating from the article 1 such as MCrAlY or thermal barrier coating (TBC), has to be removed by a process such as acid stripping, grit blasting or mechanical grinding or a combination thereof. At the same time this method also cleans the surface of the parent material from unwanted oxide layers. In addition, the surface of the crack or gap may be cleaned from oxides by a dynamic Fluoride-Ion-Cleaning (FIC) process, which is widely known in state of the art. The FIC process removes oxide layers composed of the stable Al_2O_3, Cr_2O_3 etc. oxides and depletes Al and Cr from the surface, thereby improving the braze flow and the repair of the cracked components. The process subjects the oxidized (and sulphidized) components to a highly fluorising and reducing gaseous atmosphere of hydrogen and hydrogen fluoride at high temperatures, which may vary from 900°C to 1000°C. Such FIC-processes are disclosed, for example, in EP-B1-34041, US-4,188,237, US-5,728,227 or in US-5,071,486. After successful completion of the brazing repair with braze paste and/or braze tape or Pre-sintered Braze Sheets according the invention, the component will be re-coated.

In order to braze the crack or gap it is filled with a pastes made of braze alloy. The crack or gap has a maximum width of 1000 μm. The braze paste will be

applied into and over the crack or gap before applying the heat treatment. Another possibility is to apply a presintered braze sheet or braze tape on the part to be repaired. The table 1 shows the content of different alloys used for experimental purpose.

Chemical Composition of braze-alloy (wt.-%)

Braze Alloy	Ni	Co	Cr	Al	Ta	B	Y
1	bal.	10	10	4.5	3.0	2.5	0.1-0.2
2	bal.	10	15	5.5	3.0	2.5	0.1-0.2
3	bal.	10	15	5	3.5	2.5	0.3
4	bal.	10	10	5.5	3.0	2.5	0.1-0.2

Tab. 1

In order to improve the oxidation resistance of commercially available pre-sintered braze sheets the chemical composition of the currently used and commercially available braze alloy has been modified. The aluminum content of the braze alloy has been increased to a range of between 4.5 to 6 wt.-% in order to guarantee an overall aluminum content in the matrix phase of the brazed presintered sheet of about 5 wt.-%. The γ-matrix must contain a minimum of 12wt.-% Cr. The 10-13 vol.-% Cr-rich borides in the presintered braze sheet material act as an additional Cr-reservoir, so that the overall Cr content in the material is approximately 15 wt.-%.

The overall Cr content in the pre-sintered braze sheet material should not be lower than 15 wt-%. Chromium decreases the critical Aluminium content, which is necessary for the formation of dense and stable Al oxide scale. The Al/Cr ratio in a Nickel-based alloy determines the oxidation mechanism. The limit for forming a stable oxide layer at lower temperatures requires an increase Al content.

Yttrium has also been added in small amounts to the pure braze alloy in order to improve the adhesion of the surface oxide scale on top of the braze or sheet-material. The Yttrium oxides mainly sit at the grain boundaries in the

outer Al and Cr oxide scale as the solubility of Yttrium within Cr-Al oxides is very low. The Yttria slows down diffusion along the grain boundaries, which results in an inward growth of the oxide. An inward oxidation avoids the formation of voids at the base material/oxide scale interface as no elements from the base material diffuse into the oxide. The stresses during oxide scale growth are therefore reduced and the oxide scale is less prone to spallation. The typical amount of Yttrium in oxidation resistant alloys is between 0.1 – 0.3 wt%.

Boron has a strong influence on lowering the melting point of braze alloys. Boron depresses the melting point significantly under 1200°C.

In general, elements such as Boron, Silicon, Hafnium, Zirconium can be used as Melting Point Depressant (MPD), but Boron is the favorable candidate to be used as the Melting Point Depressant, very little Boron (approx. 2.5 wt.-% boron) is needed to significantly depress the melting point of superalloys.

Chromium together with Aluminum in the braze alloy results in a good oxidation resistance of the braze-repaired area. The Chromium to Aluminum ratio should be a maximum of favorably lower than 3. Chromium as a strong solid solution hardening element increases the strength of the braze alloy. Thus, the sum of Cr and Al should be at least 15 wt.-%.

The stability of the γ/γ'-microstructure is strongly dependent on the Aluminum and Tantalum content. Ta stabilizes the gamma prime at elevated temperatures. An increasing Ta content shifts the gamma prime solvus line to higher temperatures. It is possible to design the microstructure of the brazed joint after the brazing cycle, which means without any MPD Boron by considering the sum of the Al and Ta content. Thus, the sum of Al and Ta should be at least 7.5wt.-%

Experimental results

From the above mentioned braze alloy according to Tab. 1, two batches of pre-sintered braze sheet using commercially available superalloy filler materials have been produced. The pre-sintered braze sheets are made of the braze tapes which are composed of a mixture of 40% of braze alloy and 60% filler powder through executing appropriate thermal pre-sintering cycles. The pre-sintered sheets are free of binder and shall exhibit a very low grade of porosity.

Corresponding modified pre-sintered braze sheets have been long-term exposed at 950°C for 1000h and 1600 h. Fig. 2 shows as a reference the microstructure after long-term exposure of a standard braze-sheet. Fig. 3 and 4 show in contrast the oxidation attack on the different modified braze sheet materials.

All new modified PSP material do not show any measurable internal oxidation attack compared to the currently commercially available ones. It is assumed that the increased Aluminium content in combination with the balanced Cr/Al ratio in the matrix of the presintered braze sheet material guarantees a stable and dense oxide scale. After 1000h at 950°C it was not possible to determine a significant difference in oxidation attack between each modified presintered braze sheet material. After 1600h at 950°C it was still not accurately possible to determine a significant difference in oxidation attack between the modified presintered braze sheet material. However, the batch with the braze alloy No. 2 has been measured to show the lowest oxidation attack.

The excellent oxidation properties are related to the homogeneous microstructure of the new Pre-sintered braze-sheets which comprises of a γ/γ'-matrix and two types of borides and carbides, a Cr-rich boride and a Cr,- Mo,- W-rich boride/carbide phase. The Cr and Al content in the γ/γ'-matrix is sufficiently high and the ratio between both elements is balanced in order to form a stable and dense oxide layer at the outer pre-sintered braze-sheet surface.

The physical properties of the PSP material such as the Young's modulus and the coefficient of thermal expansion (CTE) versus temperatures mainly determine the residual stresses at the PSP/parent metal interface. Therefore, the physical properties are desired to match well with the parent material. The Young's Modulus and the CTE have been measured for the newly modified pre-sintered braze sheets. Several sheets have been brazed on top of each other and subsequently test specimens have been taken for tensile tests and CTE measurements. The outcome of the tests showed that the Young's Modulus and the CTE as a function of temperature is in the same order of magnitude with most of the commonly and widely used Nickel-based superalloys.

While our invention has been described by an example, it is apparent that one skilled in the art could adopt other forms. Accordingly, the scope of our invention is to be limited only by the attached claims.

REFERENCE NUMBERS

1	Article
2	Blade
3	Platform
4	Cooling holes
5	External surface of article 1
6	Layer of MCrAlY

CLAIMS

1. Braze alloy consisting of (wt.-%) 10-15% Cr, 4.5-6% Al, 0.05-0.3% Y, 8-12% Co, 0-4% W, 2.5-5% Ta, 2.0-3.5% B with Cr+Al > 15%, Cr/Al ≤ 3 and Al+Ta > 7.5 %, Rest Nickel and unavoidable impurities.

2. The use of the brazing alloy according to claim 1 in pure form as a paste and foil or as a blend paste, as a braze tape or as a pre-sintered braze sheet.

3. A pre-sintered braze sheet, braze tape or blend paste comprising a mixture of filler material consisting of a nickel or cobalt superalloy and the braze alloy according to claim 1.

4. The pre-sintered braze sheet, braze tape or blend paste according to claim 3, wherein the mixture comprises at least 30wt.-% braze alloy.

5. The pre-sintered braze sheet, braze tape or blend paste according to claim 3 or 4, wherein the pre-sintered braze sheet braze tape or a paste contains no binder.

6. A method of repairing an article (1) comprising the step of brazing the article (1) with the braze alloy according to claim 1.

7. A method of repairing an article (1) comprising the step of brazing the article (1) with a pre-sintered braze sheet, braze tape or blend paste according to claim 3.

8. The method according to claim 6 or 7, wherein a used gas turbine component in need of repair is brazed.

ABSTRACT

The invention relates to a braze alloy consisting of (wt.-%) 10-15% Cr, 4.5-6% Al, 0.05-0.3% Y, 8-12% Co, 0-4% W, 2.5-5% Ta, 2.0-3.5% B with Cr+Al > 15%, Cr/Al ≤ 3 and Al + Ta > 7.5%, Rest Nickel and unavoidable impurities and to a use of the braze alloy in braze tape or in a pre-sintered braze sheet.

(Fig. 3)

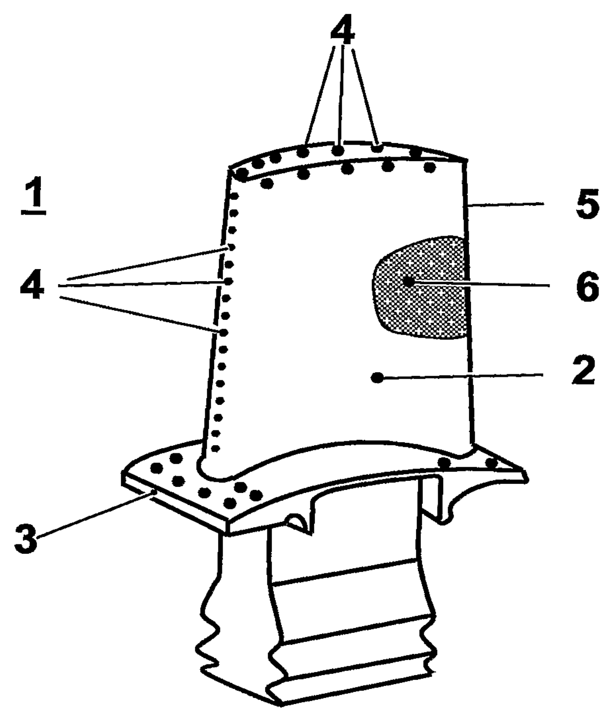

Fig. 1

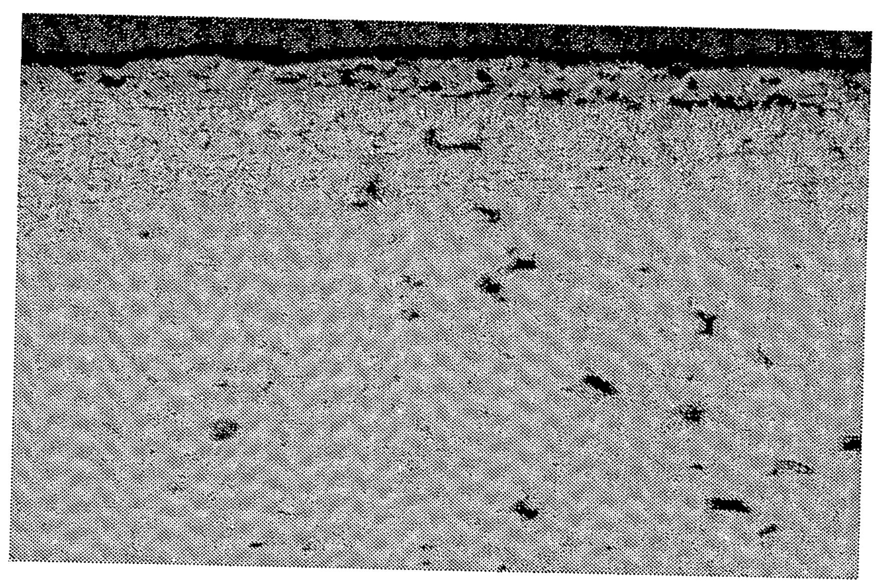

Fig. 2

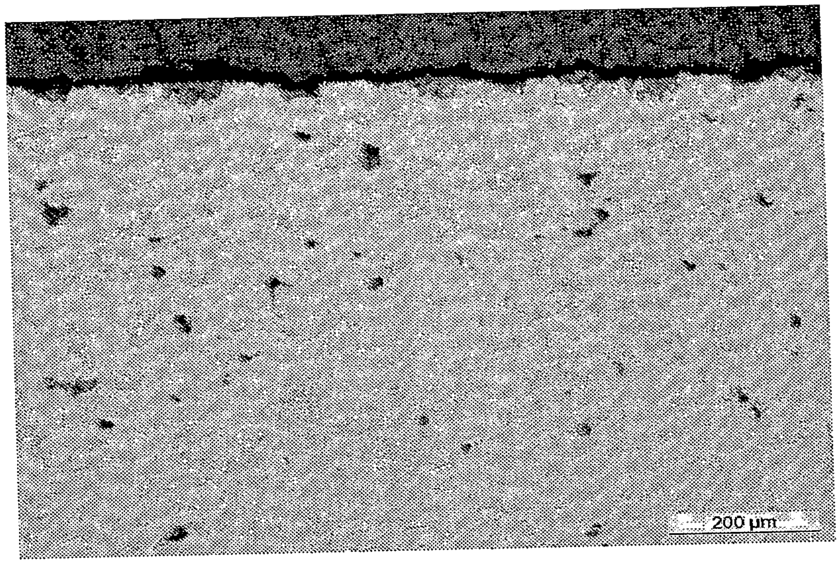

Fig. 3

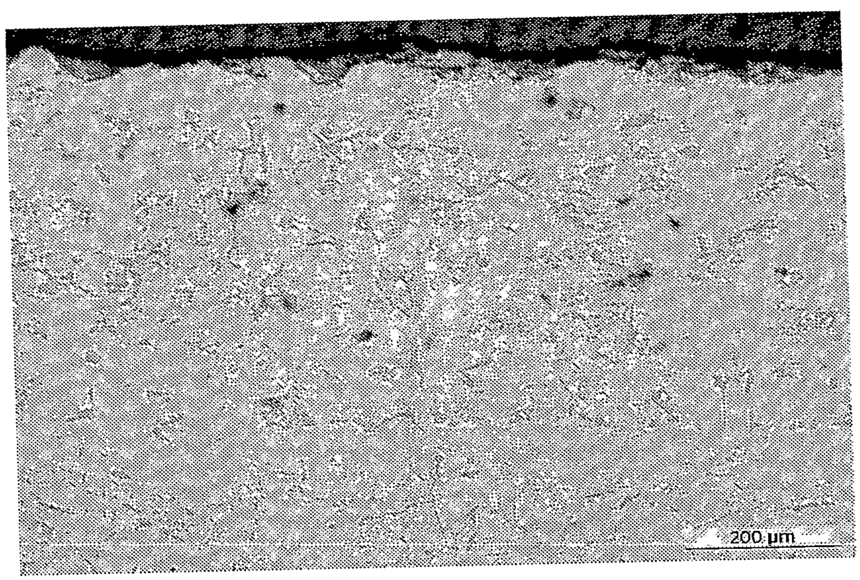

Fig. 4